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NASA TECHNICAL MEMORANDUM

NASA TM-76952

APPLICATION OF ORGANIC POLYMER SOLID ELECTROLYTES

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Translation of "Kobunshi", (High Polymers, Japan), Vol. 30, No. 11., November 1981, pp. 834-837

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 SEPTEMBER 1982

(NASA-TM-76952) APPLICATION OF ORGANIC SOLID ELECTROLYTES (National Aeronautics and Space Administration) 14 p HC A02/MF A01 CSCL 11G
N83-16524
Unclas
G3/27 02458

ORIGINAL PAGE IS
OF POOR QUALITY

STANDARD TITLE PAGE

1. Report No.
NASA TM-76952

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Application of Organic Polymer Solid Electrolytes

5. Report Date
September 1982

6. Performing Organization Code

7. Author(s)
Satoshi Sekido

8. Performing Organization Report No.

10. Work Unit No.

9. Performing Organization Name and Address
Leo Kanner Associates, Redwood City, California, 94063

11. Contract or Grant No.
NASw- 3541

13. Type of Report and Period Covered
Translation

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Kobunshi", (High Polymers, Japan), Vol. 30, No. 11, November 1981, pp. 834-837

16. Abstract

17. Key Words (Selected by Author(s))

18. Distribution Statement
Unclassified - Unlimited

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages

22. Price

APPLICATION OF ORGANIC POLYMER SOLID ELECTROLYTES

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1. Introduction /834*

When solid electrolytes are defined as crystalline solids with high ionic conductivity, virtually no polymer materials are contained in that category. When ions are considered, in the broad sense, to be solid material which transport electric charges, polymer materials would be included in that category, and interesting applications which skillfully bring out the inherent properties have been seen. This paper adopts the broad definition from such a perspective. It introduces the current state of application, discusses which properties have been used, and considers future prospects.

2. Current Applications

2.1 Application to sensors

The ion concentration sensor is an example of application to sensors. The structure is as illustrated in Figure 1. In this structure, one side (inside) of a solid electrolytic membrane is exposed to a known solution whose ionic concentration is to be measured, and electrodes are immersed in that solution. This sensor and an electrode (not illustrated in Figure 1. The same type of electrode as a conventional internal electrode is used.) are immersed in the measurement structure, and the ionic concentration C_A to be measured is determined by

$$E=E_0+(RT/Z_AF)\ln(C_A+\kappa C_B{}^{Z_A/Z_B}) \qquad (1)$$

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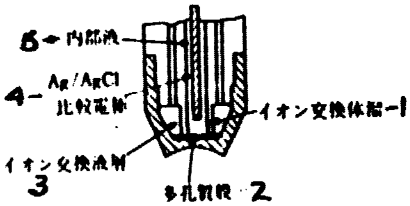
upon measurement of the electromotive force E which is generated between two electrodes. In the figure, E_0 is the standard potential (V), R is the gas constant, Z_A and Z_B are the ionic values of the measured ion and the interfering ion, F is the Faraday constant, and κ is the constant based on the type of membrane termed the selectivity coefficient. The solid electrolyte permits passage only of specific ions, and electromotive force which is dependent on the equilibrium ionic concentration and the movable ions is generated. Table 1 illustrates the relation between the types of detector ions and the electrolyte membrane used as well as the interfering ions used. These organic materials are used when written as liquid ion exchange membranes. Material insoluble in water with a movable exchange substrate which can replace the detector ions is impregnated in a mat and used. In addition, the impregnation of varinomycin, a macrocyclic antibiotic, in glass sintered membranes has been reported to result in selectivity which is approximately 750 times greater while the selectivity of K^+ to Na^+ is approximately 20 in potassium glass [1,2].

In this way, organic electrolytes have the same action as inorganic salt electrolytes through achievement of an exchange equilibrium with specific ions, and since inorganic substances cannot produce insoluble electrolytes, organic substances are capable of measurement of the ionic concentrations of No_3-, BF_4-, ClO_4- and Ca^{2+}, which had been previously impossible to measure. Another feature is the high selectivity to K^+ ion concentration.

2.2 Application to Batteries

Two types of batteries are introduced here. The initial example uses lithium as the cathode while a charge-transfer complex of organic material and iodine is used in the anode. Non-ionic poly-2-vinyl pyridine [3] and ionic n-butyl iodide pyridium [4] are used as the organic material. Both complexes are used in solution, but the former is a polymer which is used as is to raise the viscosity while the latter is used in solid form following adsorption on silica gel. Both cells are formed by direct contact between the anode material and lithium during production, and the structure is simpler than that of cells using solution electrolyte, and thin cells are produced with greater ease. In addition, the output energy density can be raised in comparison to other cells, as illustrated in Table 2, since large amounts of high energy active material can be packed in the volume occupied by the separator. The electrolyte is formed chemically through contact or electrochemically through subsequent discharge. The form in which organic material participates is not yet clear, but the internal resistance is far lower than when the electrolyte is only LiI.

Figure 1. Structure of ion concentration sensor used in solution ion exchange membrane



1 ion exchange pool
2 porous membrane
3 ion exchange solution layer
4 Ag/AgCl comparative electrode
5 internal solution

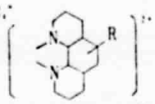
Since solid electrolyte permits passage only of specific /835
ions, when used in batteries, only the reaction required by the battery can be carried out, and a battery with low self discharge

could be produced. Actually, low values below 5% can be achieved for 10 years in such batteries of 2.5 mm thickness, and low values below 15% can be achieved in batteries of 1.0 mm thickness.

The load current has been markedly reduced with the advent of the c-MOS circuit and liquid crystal display, and features such as higher energy density and lower self discharge have been realized. These have been used as the power source in heart pacemakers, RAM back-ups, electronic watches, and desk-top calculators etc.

Table 1. Principal properties of ion selective membrane electrodes

第1表　主要イオン選択膜電極の特性

1 選択イオン	2 膜の組成	3 測定範囲	4 使用温度	5 pH範囲 応答時間	6 妨害イオン（選択係数）
	ガラス 7				
Na^+	NAS_{11-18}	~10^{-6}M	0~60°C		$Ag^+>H^+\gg Na^+\gg Li^+>K^+>NH_4^+$ Na/K 2800, H/Na 35.7
K^+	NAS_{27-5}　KAS_{27-5}	~10^{-6}M	〃		$H^+>Ag^+>K^+$, $NH_4^+>Na^+>Li^+$ K/Na 20
Ag^+	$NAS_{28.8-19}$ 11-18	〃	〃		Ag/H 10^5 Ag/Na 10^3
	含沈結晶膜 8				
S^{2-}	Ag_2S	10^0~10^{-17}M	0~50°C	~pH12 1 min	CN^-
F^-	LaF_3, NdF_3, PrF_3	~10^{-6}M	–	~pH8	OH^-, Al^{3+}, Fe^{3+}（錯形成） 9
Cl^-	$AgCl/Ag_2S$	10^0~5×10^{-5}M	0~50°C	pH3~11 2sec	CN/Cl 5×10^6, I/Cl 2×10^6 NO_3/Cl 5-9, Br/Cl 3×10^2
Br^-	$AgBr/Ag_2S$	10^0~10^{-5}M	0~50°C	pH1.5~11.5 2sec	CN/Br 1.5×10^4, I/Br 5×10^3
I^-	AgI/Ag_2S	10^{-1}~10^{-7}M	0~50°C	pH2~11 20sec	CN^-, S^{2-}, MnO_4^-
Ag^+	Ag_2S	10^0~10^{-17}M			Hg^{2+}
CN^-	10 AgXの表面にAg_2S膜を作る ネルンスト式から求まるX濃度の2倍をとる	10^{-2}~10^{-6}M			S^{2-}, I^-, MnO_4^-
SCN^-	$AgSCN/Ag_2S$	10^0~10^{-5}M			I^-, Cl^-, 強還元剤 11
SO_4^{2-}	$BaSO_4$	10^{-1}~10^{-4}M			Cl^- 10^{-3}M以上妨害 12 ・Ag_2S膜を表面に作ると下げられる 13
	混合結晶膜 − 14				
Zn^{2+}	$ZnS+Ag_2S$				
Cu^{2+}	$CuS+Ag_2S$	10^{-1}~10^{-5}M	0~50°C	30sec	Na/Cu 5×10^{-4}, Fe/Cu 140 Hg^{2+}, Ag^+
Cd^{2+}	$CdS+Ag_2S$	10^{-1}~10^{-7}M			Ag^+, Cu^{2+}, Hg^{2+}
Pb^{2+}	$PbS+Ag_2S$	10^{-1}~10^{-7}M			〃
15 2価カチオン	Ag_2Sより大きな溶解度をもつ塩$+Ag_2S$ 16				
	液体イオン交換膜 17 可動交換基				
Cl^-	NR_4^+	10^{-1}~10^{-5}M	〃　〃	2~11	ClO_4^-/Cl^- 32, I^-/Cl^- 17, NO_3^-/Cl^- 4.2
NO_3^-	Ni  $^{2+}$			2~12	I^-/NO_3^- 20, ClO_4^-/NO_3^- 10^3, ClO_3^-/NO_3^-
BF_4^-					I^-/BF_4^- 20
ClO_4^-	Fe（〃）$^{2+}$	10^0~10^{-5}		4~10	OH^-/ClO_4^- 1.0
Cu^{2+}	$R-S-CH_2-CO_2^-$	10^{-1}~10^{-5}		4~7	Fe^{2+}/Cu^{2+} 1400, H^+/Cu^{2+} 10
Pb^{2+}		10^{-2}~10^{-5}		3.5~7.5	Cu^{2+}/Pb^{2+} 2.6
Ca^{2+}	$(RO)_2PO_2^-$	10^0~10^{-5}		5.5~11	H^+/Ca^{2+} 10^7, Zn^{2+}/Ca^{2+} 3.2
Ca & Mg		10^0~10^{-8}			Zn^{2+} 3.5, Fe^{2+} 3.5, Cu^{2+} 3.1, Ni^{2+} 1.35
18	酵素（ガラス電極を使うマトリクス中に固定） 19				
尿素	ウレアーゼ（[illegible]）				
グルタミン	20 〃				
アスパラギン	〃				
アミノ酸	〃				

1 selected ion 2 composition of membrane
3 measurement range 4 temperature used
5 pH range, response time 6 interfering ion (selectivity coefficient)
7 glass
8 impregnated crystalline membrane
9 (forming complex)
10 An Ag_2S membrane is formed on the surface of AgX and a value of double the concentration of X determined from the Nernst formula is assumed
11 strong reduction agent
12 interference above $Cl^-10^{-3}M$
13 *declines when an Ag_2S membrane is formed on the surface
14 blended crystalline membrane
15 divalent cation
16 salt with solubility greater than that of Ag_2S + Ag_2S
17 liquid ion exchange membrane movable exchange group
18 oxygen, glutamine, asparagin, amino acid
19 oxygen (fixed in matrix covering glass electrode)
20 urease (acrylamide)

2.3 Application to Elements Applying Electrical Double Layer Capacity

Electrodes of carbon or chalcogen compounds of the following metals are formed on both surfaces of Ag^+ or Cu^+ ion conducting solid electrolytes, and conducting ions move in electrolyte when direct current voltage is applied under decomposition voltage of electrodes or electrolyte, resulting in precipitation on the cathode. Anions become excessive near the anode, and a positive charge equivalent to the excess charge accumulates at the anode, forming an electrical double layer.

The equivalent series resistance becomes negligible when electrolyte with high ion conductivity and a low electron transport rate is used. Stabilization to room temperature is /836
conducted by ion exchange of an α-CuI type structure with high ion conductivity in Ag^+ or Cu^+ ion conducting electrolyte to produce such an electrolyte. Many such organic compounds have been examined, as illustrated in Tables 3, 4 and Figure 4. However, an organic compound with ion conductivity and thermal stability superior to those of inorganic solid electrolytes has not been obtained at present [5-24]. The capacity density of the electrical double layer produced as a result is very great since

solid electrolytes are composed only of ions. For example, when active carbon electrodes are used in Cu^+ ion conducting electrolytes, values of approximately 30 F/g per unit capacity of electrode are achieved, while the result when Cu_2S electrodes are used is approximately 300 F/g. The oxygen adsorbed on active carbon electrodes contributes slightly in side reactions, but the Faraday reaction tends not to occur although the potential range is narrow in Cu_2S electrodes, and superior potential retention is exhibited. Resistance of the dissolution reaction and precipitation of the opposing electrode pose problems in the case of producing potential recording elements or capacitors applying the electrical double layer capacity, while electrode material which would minimize this has been examined in capacitors, but separate electrodes (standard poles) which are not conducting have been used in potential recording elements [25,26].

Table 2. Comparison of performance of various types of coin cells (diameter 23 mmφ, thickness 2.5 mm)

第2表　各種コイン型電池の性能比較 (径23 mmφ 厚さ 2.5 mm)

1 電池の種類	Ag_2O-Zn	AgO-Zn	2 有機電解質リチウム	3 固体電解質	
				P2VPIn	BPI_{17}
4 開路電圧 (V)	1.5	1.5	3.0	2.8	2.8
5 エネルギー密度 (mWh/cc)	345	480	400～460	470	485
6 自己放電 (%/期間)	13 7～10/年	13 7～10/年	13 5/5年	13 5/10年	13 5/10年
7 最適負荷電流	mA 以上 14	mA 以上 14	数百μA 15 以下	10μA以下 16	10μA以下 16
8 耐漏液性	17 中	中	中	中	18 大
9 薄型化の容易さ	17 中	中	中	18 大	19 最大
10 電圧平坦性	○	○	MnO_2 $(CF)_n$ △ ○	△△△	△△△
11 公害性	△△	△△	○	○	○
12 材料コスト	20 高	高	17 中	中	中

1 type of battery
2 organic electrolyte lithium
3 solid electrolyte
4 open circuit voltage
5 energy density
6 self discharge
7 optimum load current
8 leakage resistance
9 ease of making thinner
10 flatness of voltage
11 pollution
12 cost of material
13 years
14 above

15 below several hundred µA
17 moderate
19 greatest

16 below 10 µA
18 great
20 high

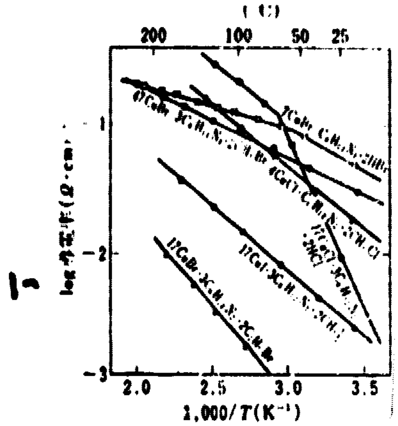
Table 3. Organic Ag^+ ion conducting solid electrolytes

Conductors	mole ratio	stable range	temp. (°C)	Conductivity (s cm^{-1})	reference
$RbAg_4I_5$		26<	<145	0.25~0.27	5)~7)
$n(CH_3)_4NI \cdot mAgI$	13/87 2/13		<181	0.041~0.046 0.01	7)~10), 16), 17)
$n(CH_3)_2(C_2H_5)_2NI \cdot mAgI$	13/87			0.061	16)
$n(C_2H_5)_4NI \cdot mAgI$	12/88		<116	0.022~0.025	7)~10), 16), 17)
$nC_5H_5NHI \cdot mAgI$	1/5 1/8			0.085 0.011	11)~16) 12), 16)
Dimethylpyrollidium	1/7			0.07	16)
Benzyltrimethyl-ammonium	1/8			0.01	16)
Methane-1, 1-bis-methyldiethylammonium	1/6		[illegible]	0.05	16)
Octamethylenetri-ammonium	3/22			0.06	16)
1-methyl-1-thioniacyclo-hexane	1/7			0.06	16)
Isopropyldimethyl sulphonium	1/7			0.07	16)
n 4-methylpyridinium-mAgI	1/5 1/7			0.016 0.050	12)
n 3-methylpyridinium-mAgI	1/7			0.012	12)
n 2-methylpyridinium-mAgI	1/7			0.019	12)
n 4-NH_2-pyridinium-mAgI	1/16			0.026	12)
n 1-C_2H_5-pyridinium-mAgI	1/7 1/8			0.020 0.012	12)
$n(CH_3)_3SI \cdot mAgI$	1/6		<198	0.01	17)
$n(CH_3)_2S(CH_2)_6S(CH_3)_2 2I \cdot mAgI$	7/93		<116	0.01	17)
n Quinoline HI·mAgI	1/8			0.015	12)
n isoquinoline HI·mAgI	1/8			0.017	12)

3. Role of Polymer Electrolytes

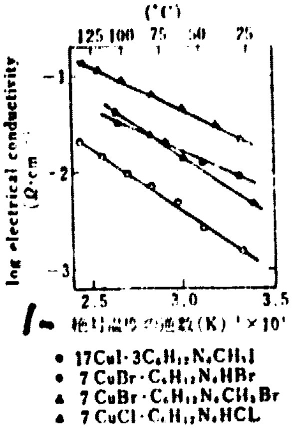
The role of polymer electrolytes will be singled out from the aforementioned applications. First, even if there are many coexisting ions due to selective ion transmission, a sensor which responds only to specific ions therein would be identical with inorganic substances in terms of high purity, high density electrolysis, water treatment or production of a battery with little self discharge. Measurement of ions which could not be measured in inorganic substances is possible by producing material which does not dissolve in an aqueous solvent, and a membrane with high sensitivity and high selectivity can be produced. Rapid movement of ions in electrolyte is required in electrolysis, batteries or elements applying electrical double layers. Many attempts at ion exchange using organic macroions have been made to produce materials with such high ionic conductivity, but at present, only materials which are somewhat /937 inferior to inorganic materials in terms of ionic conductivity and thermal stability have been produced. The reasons for the inferiority of ionic conductivity include the fact that only crystals with a high site occupation rate and high number of mobile ions have been produced, and interference of shift of mobile ions by massive organic cations [17]. Recently, attention has been directed to reports of halogen conductivity in complexes of crown ether or straight chain polymer ether and metal halides which are firmly linked with cations, thereby weakening the bond with anions [27,28]. Among these, complexes of dibenzo 18 cap 6 ether and LiX have the greatest conductivity with Cl^- among halogens as seen in Table 4, and have conductivity of 4.38 x $10^{-4}scm^{-1}$ even at room temperature. High ionic conductivity may be realized through polymers if the effect of complex formation rather than simple ion exchange is added.

Figure 2. Conductivity of CuX-halide alkyl triethylene diamine Cu^+ ion conducting electrolyte



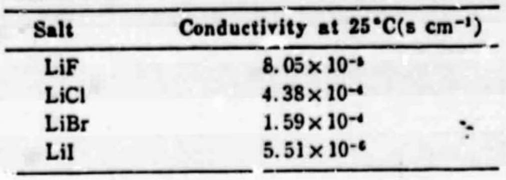
1-log of conductivity

Figure 3. Conductivity of CuX-halide alkyl hexamethylene tetramine Cu^+ ion conducting electrolyte



1-logarithm of absolute temperature $(K)^{-1}$ x 10^3

Table 4. Organic halogen conducting solid electrolyte



Salt	Conductivity at 25°C(s cm^{-1})
LiF	8.05×10^{-5}
LiCl	4.38×10^{-4}
LiBr	1.59×10^{-4}
LiI	5.51×10^{-6}

4. Conclusion

The production of ion conducting materials using polymers and their application have just begun along with research in affiliated regions. Phenomena related to ions which are of considerable interest have been seen in bio-polymer membranes, although not touched upon in this paper. Polymer electrolyte of necessity would be produced, with expansion of unique applications as this research proceeds.

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